Herbicide Sorption Coefficients in Relation to Soil Properties and Terrain Attributes on a Cultivated Prairie

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The sorption of 2,4-D and glyphosate herbicides in soil was quantified for 287 surface soils (0–15 cm) collected in a 10 × 10 m grid across a heavily eroded, undulating, calcareous prairie landscape. Other variables that were determined included soil carbonate content, soil pH, soil organic carbon content (SOC), soil texture, soil loss or gain by tillage and water erosion, and selected terrain attributes and landform segments. The 2,4-D sorption coefficient (K_d) was significantly associated with soil carbonate content (−0.66; $P < 0.001$), soil pH (−0.63; $P < 0.001$), and SOC (0.47; $P < 0.001$). Upper slopes were strongly eroded and thus had a significantly greater soil carbonate content and less SOC compared with lower slopes that were in soil accumulation zones. The 2,4-D K_d was almost twice as small in upper slopes than in lower slopes. The 2,4-D K_d was also significantly associated with nine terrain attributes, particularly with compounded topographic index (0.59; $P < 0.001$), gradient (−0.48; $P < 0.001$), mean curvature (−0.43; $P < 0.001$), and plan curvature (−0.42 $P < 0.001$). Regression equations were generated to estimate herbicide sorption in soils. The predicted power of these equations increased for 2,4-D when selected terrain attributes were combined with soil properties. In contrast, the variation of glyphosate sorption across the field was much less dependent on our measured soil properties and calculated terrain attributes. We conclude that the integration of terrain attributes or landform segments in pesticide fate modeling is more advantageous for herbicides such as 2,4-D, whose sorption to soil is weak and influenced by subtle changes in soil properties, than for herbicides such as glyphosate that are strongly bound to soil regardless of soil properties.

Pesticide fate models are being used in regional assessments of the risk of pesticide movement by leaching, runoff, and water-eroded soil (Stewart and Loague, 1999; Eason et al., 2004; McQueen et al., 2007). Sorption coefficients (measures of pesticide sorption by soil) are among the most sensitive input parameters in pesticide fate models. It has been demonstrated that sorption coefficients (K_d) vary within soil landscapes due to differences in soil organic carbon (SOC) content or soil pH between slope positions (Novak et al., 1997; Farenhorst et al., 2003). Establishing methods to account for this variation could reduce uncertainties in regional-scale assessments of pesticide fate (Dubus et al., 2003). The recent integration of digital terrain models (MacMillan and Pettapiece 2000) with the National Soil Database of Canada (NSDB) (SLC version 3; Agriculture and Agri-Food Canada, 2005) allows for quantitative information on the spatial variability of soil properties within soil landscapes of NSDB map units. Because soil properties influence K_d values, it is worthwhile to further explore the use of digital terrain modeling as a tool to predict the distribution of sorption coefficients within map units of soil databases.

Two herbicides were selected: glyphosate (*N*-phosphonomethylglycine) and 2,4-D (2,4-dichlorophenoxyacetic acid). Glyphosate is a nonselective post-emergent herbicide that is increasingly being used in North America because of the expanding cultivation of glyphosate-tolerant crops. Glyphosate phytotoxicity is rapidly inactivated in soils due to the strong sorption of the herbicide (Sprankle et al., 1975). Glyphosate sorption by soil increases with decreasing soil pH (De Jonge and de Jonge, 1999). Typically, neither glyphosate nor its metabolites persist

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Abbreviations: A, aspect; CTI, compounded topographic index; G, gradient; K_d, sorption coefficient; K_{oc}, soil organic carbon sorption coefficient; MEAN, mean curvature; NSDB, National Soil Database of Canada; PLAN, plan curvature or horizontal curvature; PROFILE, profile curvature or vertical curvature; SCA, specific catchment area; SDA, specific dispersal area; SPI, stream power index; SOC, soil organic carbon content; Z, elevation.

Table 1. Description of terrain attributes.

Terrain attribute	Abbreviation (units)	Description
Elevation	Z (m)	Elevation above sea level.
Gradient	G (degrees)	Slope between the land surface and a horizontal plane at a given point.
Aspect	A (degrees)	Orientation of the slope face with respect to True North.
Profile curvature or vertical curvature	PROFILE (degrees m^{-1})	Down-slope curvature of a slope segment. Convex curvatures are assigned positive values; concave curvature are assigned negative values.
Plan curvature or horizontal curvature	PLAN (degrees m^{-1})	Across-slope or contour curvature of the slope segment. Convex curvatures are assigned positive values, and concave curvature are assigned negative values.
Mean curvature	MEAN (degrees m^{-1})	The average of normal section curvature. Mean-convex curvatures are assigned positive values; mean-concave curvature are assigned negative values.
Specific catchment area	SCA (m^2 m^{-1})	The area upslope of a contour segment that contributes flow to that segment divided by the length of the segment.
Specific dispersal area	SDA (m^2 m^{-1})	The area downslope of a contour segment that can receive flow from that segment divided by the length of the segment.
Compounded topographic index	CTI = ln(SCA/G)	The ratio between the catchment area and slope to reflect flow accumulation.
Stream power index	SPI = SCA × G	The erosive power of the terrain.

in the environment (Vencill, 2002), but Nomura and Hilton (1977) reported glyphosate half-lives of up to 22 yr in soils with pH <6 and organic matter contents of over 90 g kg^{-1}. The number of reports on the transport of glyphosate in the environment is limited, but an older study suggests that the herbicide is relatively immobile in soils (Rueppel et al., 1977).

2,4-D is a foliar-applied herbicide with soil-residual activity that can control broadleaf weeds in annual and perennial grass systems. 2,4-D is increasingly being used as a pre-seed burn off treatment to control glyphosate-tolerant canola volunteers (Simard and Legere, 2002). Despite the short half-life of 2,4-D in soil, the herbicide has been found in surface waters and ground waters throughout North America (Hallberg, 1989; Goodrich et al., 1991; Kolpin et al., 1995; Cessna and Elliot, 2004). Sorption of 2,4-D by soil is largely the result of weak hydrogen bonds and van der Waals interactions with soil organic matter (Calvet, 1989; Senesi, 1992). Other soil properties, including alkalinity and clay content, are known to affect 2,4-D sorption (Reddy and Gambrell, 1987; Gaultier et al., 2006).

Previous research demonstrated that the addition of terrain attributes (Table 1) to data on soil properties improved the prediction of 2,4-D sorption coefficients within a zero-tilled, undulating to hummocky, calcareous prairie landscape (Farenhorst et al., 2003). The objective of this research was to examine whether terrain attributes or landform segments are useful in assessing the distribution of 2,4-D and glyphosate sorption within a heavily eroded, undulating, calcareous prairie landscape.

Material and Methods

Study Site and Soil Analyses

The study site is an agricultural field in Nora Township, Pope County (SW-1/4–31–126N-40W) near Morris, Minnesota. The site and its surrounding area is characterized by undulating topography with slopes <6°. The field has been under cultivation for approximately 100 yr and has been moldboard plowed on an annual basis for at least 40 yr. Wheat, soybean, and corn are grown, but wheat has been the predominant crop in the past 5 yr. Several herbicides, including 2,4-D, have been applied to the field during this time.

Two hundred eighty-seven soil samples (0–15 cm) were collected in a 10 × 10 m grid in a 2.72-ha section of the field. Samples were collected in August 2000 using a 3-inch (7.6-cm) Giddings hydraulic probe. Points were referenced (latitude, longitude, and elevation) using a Trimble AG132 DGPS unit with differential corrections (OmniSTAR, Houston, TX). A grid design was selected because of its simplicity and because it required little initial field investigation. The grid spacing was sufficient to capture the shorter-interval variability of the undulating terrain.

The 287 samples were air-dried and passed through a 2-mm-mesh sieve. Samples were analyzed for SOC, soil pH, soil carbonate content (calcite and dolomite), and herbicide sorption. In addition, 44 samples were randomly chosen to measure soil texture by the hydrometer method (Gee and Bauder, 1986). For the SOC analyses, inorganic carbon was removed by digestion with 6 mol L^{-1} HCl followed dry combustion of 0.12 g oven-dried soil using a LECO model CHN 600 C and N determinator (LECO, St. Joseph, MI) (Nelson and Sommers, 1982). Soil pH values were obtained using 10 mL of 0.01 mol L^{-1} CaCl$_2$ and 5 g air-dried soil (McKeague, 1978). Carbonate content was determined using a volumetric calcimeter that measures evolved carbon dioxide on addition of 6 mol L^{-1} HCl · FeCl$_2$ to a soil sample (Loeppert and Suarez, 1996).

Herbicide sorption by soil was determined using batch equilibrium analysis. The 2,4-D stock solution (1 mg L^{-1} 2,4-D and 16.7 × 10^{-3} Bq L^{-1} ^{14}C U-ring–labeled 2,4-D) was prepared by dissolving analytical grade 2,4-D (95% chemical purity) (Sigma Aldrich, St. Louis, MO) and ^{14}C U-ring labeled 2,4-D (99% radiochemical purity; specific activity 9.25 MBq mmol^{-1}) (Sigma Aldrich) in 0.01 mol L^{-1} CaCl$_2$. The glyphosate stock solution (1 mg L^{-1} glyphosate and 16.7 × 10^{-3} Bq L^{-1} [phosphonomethyl-^{14}C] glyphosate) was prepared by dissolving analytical-grade glyphosate (99% purity) (Chem Service, West Chester, PA) and [phosphonomethyl-^{14}C] glyphosate (95% purity; specific activity 89 MBq mmol^{-1}) (Sigma Aldrich) in 0.01 mol L^{-1} CaCl$_2$. Herbicide solutions (10 mL) were added to soil (5 g) in Teflon tubes (duplicates) and rotated for 24 h to establish equilibrium. Samples were centrifuged at 10,000 rpm for 10 min. Aliquots (1 mL) of supernatant (duplicates) were removed from each tube and used to determine the amount of 2,4-D or glyphosate remaining in solution. The

amount of radioactivity in herbicide solutions and samples from experiments was determined using liquid scintillation counting with automated quench correction (#H method) (LS 7500; Beckman Instruments, Fullerton, CA). Radioactivity was measured using 10 mL of Scintisafe scintillation cocktail (Fisher Scientific, Fairlawn, NJ) and a maximum counting time of 10 min.

The 2,4-D or glyphosate sorption partition coefficient, K_d (L kg^{-1}), was calculated as $K_d = C_s/C_e$, where C_s is the amount of herbicide sorbed by the soil (g kg^{-1}) and C_e is the herbicide concentration of the soil solution at equilibrium (g L^{-1}). The amount of 2,4-D or glyphosate sorption per unit SOC, K_{oc}, was determined as $K_{oc} = (K_d/SOC) \times 100$.

Terrain Attributes, Landform Segments, and Erosion Estimates

A topographic survey of the sampling area was conducted on a 10×10 m grid and expanded to a larger portion of the field (16.6 ha). These data were used to establish a digital elevation model using a Gaussian variogram interpolator in Surfer version 8.00 (1993–2001; Golden Software Inc., Golden, CO). Terrain attributes were calculated for each cell as reported in Pennock (2003) and Farenhorst et al. (2003) (Table 1). Gradient (G), aspect (A), profile curvature (PROFILE), and plan curvature (PLAN) were calculated using the programs of Martz and de Jong (1988). Specific catchment area (SCA) and specific dispersal area (SDA) were calculated using the program Digital Elevation Model Networks (Costa-Cabral and Burges, 1994). The mean curvature (MEAN), compound topographic index (CTI), and stream power index (SPI) were calculated in Microsoft Excel 2002 (1985–2003; Microsoft Corporation, Redmond, WA) based on equations described in Moore et al. (1991) and Gessler et al. (1995). Each sampling point was assigned 10 computed terrain attributes (Table 1) using a Fortran program.

Landform segments were determined using the MacMillan and Pettapiece (2000) Landform Description Program written in Microsoft Visual FoxPro version 7 (1992–2001, Microsoft Corporation). Each sampling point was assigned one of three landform segments (upper-slope, mid-slope, or lower-slope), using Surfer version 8.00 (1993–2002; Golden Software Inc.) and ArcView version 3.2 (1999–2003; Environmental Systems Research Institute Inc., Redlands, CA). Although other landform segmentation models are available (Pennock, 2003), the MacMillan and Pettapiece (2000) Landform Description Program was used in this study because this is the only landform segmentation model that has been incorporated into a national soil database, the NSDB.

The estimated amount of tillage and water erosion at each sampling point was determined using the WATEM model (Van Oost et al., 2000) as implemented by Schumacher et al. (2005). Model variables were chosen to reflect the climate, management practices, topography, and soils existing on-site. Tillage practices included a moldboard plow followed by two passes of a tandem disk. A long-term corn–soybean–wheat rotation was assumed for erosion calculations. Model coefficients were k_{till} (tillage erosion coefficient) = 718 kg m^{-1} yr^{-1}, R (rainfall and runoff factor) = 0.153 MJ mm m^{-2} h^{-1} yr^{-1}, K (soil erodibility factor) = 36.9 kg m^2 h m^{-2} MJ^{-1} mm^{-1}, C (cover-management factor) = 0.21, P (supporting practice factor) = 1, and LS (slope length and steepness factor) calculated from digital elevation model output (m). By convention, negative values of soil redistribution indicate soil loss, and positive values indicate soil gain (deposition). The WATEM model has been used in our previous studies, and its estimates of water and tillage erosion were in good agreement with detailed Cesium-137 analysis in fields (Schumacher et al., 2005).

Statistical Analyses

Statistical analyses were performed in SPSS version 13.0 (2004, SPSS Inc.), Sigma Stat version 2.03 (1992–1997, SPSS Inc.), or SAS version 8.01 (2000, SAS Inst.). Because most data failed the Kolmogorov-Smirnov normality test even after transformation, the nonparametric Kruskal Wallis ANOVA on ranks was used to assess the effects of landform segments (upper slopes, mid-slopes, and lower slopes) on each of the following parameters: (i) SOC, soil pH, total soil carbonates, calcite, dolomite, clay, and sand (soil properties); (ii) soil loss or gain by tillage erosion, water erosion, and tillage and water erosion combined (erosion parameters); and (iii) 2,4-D K_d, 2,4-D K_{oc}, glyphosate K_d, and glyphosate K_{oc} (herbicide sorption coefficients). Parametric correlation and regression analyses were applied to untransformed data due to the robust nature of these analyses (Legendre and Legendre, 1998). Pearson pairwise correlation analyses were used to determine the strengths of associations between terrain attributes (Z, G, A, PROFILE, PLAN, SCA, SDA, MEAN, CTI, and SPI) (Table 1) and each of the following parameters: (i) SOC, soil pH, total soil carbonates, calcite, and dolomite (soil properties); (ii) soil loss or gain by tillage erosion, water erosion, and tillage and water erosion combined (erosion parameters); (iii) 2,4-D K_d, 2,4-D K_{oc}, glyphosate K_d, and glyphosate K_{oc} (herbicide sorption parameters). Pearson pairwise correlation analyses were used to determine the strength of associations between these soil properties and herbicide sorption coefficients and between these erosion parameters and herbicide sorption coefficients. Forward stepwise multiple linear regression analyses were performed to determine the soil properties (SOC, soil pH, total soil carbonates, calcite, and dolomite) and/or terrain attributes (Z, G, A, PROFILE, PLAN, SCA, SDA, MEAN, CTI, and SPI) (Table 1) that best predicted herbicide sorption coefficients (2,4-D K_d, 2,4-D K_{oc}, glyphosate K_d, and glyphosate K_{oc}). Variables in the model had to be significant at the 0.05 level. The most suitable model (best prediction) was determined to be the model with a relatively large R^2 value, and its Mallows' Cp statistic (Mallows, 1973) closest to the number of variables added, thereby preventing overfitting and colinearity in regression. The Mallow's Cp is defined as Cp = RSS/σ^2 − (n − 2p), where RSS = the residual sum of squares = the error sum of squares for the model with p regressors, σ^2 = the error mean square from fitting the whole model with all regressors considered, n = sample size, and p = the number of variables in the regression.

Results

Results by landform segments demonstrated that 2,4-D sorption was significantly larger in lower slopes than in mid- or upper

Table 2. Means and SDs (minimum; maximum; median) for measured variables.

	Upper slopes (*n* = 98)	Mid-slopes (*n* = 128)	Lower slopes (*n* = 61)
Sorption coefficients			
2,4-D K_d (L kg^{-1})	0.9 ± 0.4 b† (0.3; 2.0; 0.8)	1.0 ± 0.5 b (0.3; 2.6; 0.9)	1.6 ± 0.4 a (0.5; 2.6; 1.5)
2,4-D K_{oc}	91.1 ± 33.8 b (38.3; 188.9; 85.8)	107.5 ± 51.5 b (23.2; 284.6; 95.1)	139.7 ± 40.8 a (59.2; 260.2; 127.6)
Glyphosate K_d (L kg^{-1})	108.2 ± 30.6 b (63.5; 210.7; 104.8)	133.6 ± 48.7 a (58.4; 296.1; 118.3)	118.7 ± 33.9 a (79.5; 245.8; 112.2)
Glyphosate K_{oc}	11,182.8 ± 3332.4 b (3957.8; 20,037.3; 10,933.9)	14,863.2 ± 6254.7 a (4553.4; 38,160.8; 13,394.7)	10,891.3 ± 3610.6 b (4988.4; 20,830.3; 10,480.3)
Soil properties			
SOC‡ (g kg^{-1})	10.1 ± 2.5 a (4.7; 19.7; 10.2)	9.5 ± 2.6 a (3.8; 18.2; 9.1)	11.6 ± 3.2 b (5.5; 19.3; 11.3)
Soil pH	7.5 ± 0.2 a (6.9; 7.8; 7.5)	7.5 ± 0.1 a (7.2; 7.9; 7.5)	7.3 ± 0.2 b (6.9; 7.6; 7.3)
Calcite (g kg^{-1})	39.8 ± 39.6 a (0.0; 127.0; 30.6)	34.2 ± 42.4 a (0.0; 183.8; 15.7)	3.7 ± 10.0 b (0; 63.8; 0.0)
Dolomite (g kg^{-1})	32.1 ± 27.3 a (0.0; 97.6; 21.9)	24.9 ± 24.4 a (2.1; 88.1; 12.3)	10.4 ± 10.4 b (0.0; 79.0; 8.8)
Total carbonates (g kg^{-1})	71.9 ± 62.5 a (0.0; 223.4; 59.0)	59.1 ± 60.0 a (5.0; 259.2; 36.9)	14.1 ± 19.3 b (0.0; 142.8; 9.2)
Clay (%)§	16.1 ± 3.7 a (8.6; 25.2; 15.9)	16.2 ± 4.9 a (3.7; 25.5; 16.7)	14.2 ± 5.6 a (1.0; 20.1; 16.4)
Sand (%)§	44.8 ± 7.6 a (24.9; 59.1; 45.0)	47.0 ± 9.3 a (16.5; 55.0; 36.5)	47.5 ± 7.8 a (32.5; 54.4; 50.27)
Soil loss (−) or gain (+) by			
Tillage erosion (Mg ha^{-1} yr^{-1})	−12.9 ± 13.3 a (−45.7; 24.0; −13.6)	1.8 ± 15.3 b (−34.4; 53.5; 0.6)	6.0 ± 4.1 c (−5.0; 16.3; 6.6)
Water erosion (Mg ha^{-1} yr^{-1})	−14.0 ± 7.9 b (−46.1; −3.2; −13.0)	−22.0 ± 20.8 a (−48.8; 155.7; −25.0)	7.2 ± 29.2 c (−25.2; 129.4; 2.9)
Tillage and water erosion (Mg ha^{-1} yr^{-1})	−26.9 ± 15.2 a (−67.5; 10.3; −25.9)	−20.2 ± 27.8 a (−53.5; 207.3; −24.1)	13.2 ± 29.2 b (−15.5; 139.7; 8.4)

† Group means in rows with the same letter are not significantly different from each other (*p* < 0.05).

‡ Soil organic carbon.

§ Soil texture was determined for 44 soil samples only (18 samples in upper slopes, 17 samples in mid-slopes, and 9 samples in lower slopes).

slopes (Table 2). Soils of lower slopes contained significantly more SOC and were slightly less alkaline than soils of upper- and mid-slopes (Table 2). Upper- and mid-slopes had significantly greater soil carbonate contents than lower slopes (Table 2). Soil carbonate content was negatively associated with soil redistribution from tillage (−0.55; *P* < 0.001) and to a lesser extent from water (−0.22; *P* < 0.001). Soil organic carbon was positively associated with soil redistribution from tillage (0.26; *P* < 0.001) and water (0.21, *P* < 0.001). Tillage erosion decreased significantly in the sequence upper slope > mid-slopes > lower slopes (Table 2). Water erosion rates decreased significantly in the sequence mid-slopes > upper slopes > lower slopes (Table 2). Despite differences in erosion rates across slope positions, soil texture did not vary significantly across slope positions (Table 2). Overall, soil texture was relatively consistent from 0 to 40 cm depth (Farenhorst, unpublished data), so that the effect of erosion on soil properties was predominantly the change of SOC and soil carbonate content in surface soils.

The sorption of 2,4-D was significantly associated with all variables except aspect (A) (Tables 3 and 4). The strongest associations were between 2,4-D K_d and soil carbonate content (−0.66; *P* < 0.001) and soil pH (−0.63; *P* < 0.001) (Table 3). The 2,4-D sorption (Fig. 1A and 1B) was particularly small in upper slope positions of the center of the field that were characterized by alkaline soils (Fig. 1C) with large carbonate contents (Fig. 1D). The

association between 2,4-D K_d and SOC was less strong (0.47; *P* < 0.001) (Table 3), but 2,4-D K_d values (Fig. 1A) were smaller on eroded knolls (Fig. 1E) that contained lesser SOC (Fig. 1F).

The CTI provided a stronger association with 2,4-D K_d (0.59; *P* < 0.001) and 2,4-D K_{oc} (0.50; *P* < 0.001) than other terrain variables (Table 4). Smaller CTI values (Fig. 1G) reflected areas with greater tillage + water erosion (Fig. 1E; Table 4). The association between CTI and tillage erosion (0.60; *P* < 0.001) was stronger than that between CTI and water erosion (0.35; *P* < 0.001) (Table 4). 2,4-D K_d (0.53; *P* < 0.001) and 2,4-D K_{oc} (0.41; *P* < 0.001) were thus also significantly associated with tillage + water erosion, and the strengths of these associations were particularly due to the relatively strong association between 2,4-D sorption and tillage erosion (Table 3).

There were also significant negative associations between 2,4-D K_d and the terrain attributes G (−0.48; *P* < 0.001), MEAN (−0.43; *P* < 0.001), and PLAN (−0.42; *P* < 0.001) (Table 4). Tillage erosion was very well correlated with MEAN (−0.66; *P* < 0.001) and PLAN (−0.65; *P* < 0.001) but to a lesser extent with G (−0.18; *P* < 0.01) (Table 4). Water erosion was significantly correlated with G (−0.53; *P* < 0.001) but not with MEAN or PLAN (Table 4). Predictions of 2,4-D sorption coefficients were equally strong when soil properties alone or terrain variables alone were used (Table 5).

Table 3. Pearson correlation coefficients for determining the association between sorption coefficients (K_d) and a range of independent variables.

Independent variables	Glyphosate K_d	Glyphosate K_{oc}†	2,4-D K_d	2,4-D K_{oc}
Soil properties				
SOC‡	ns	−0.52***	0.47***	−0.12*
Soil pH	−0.21***	ns§	−0.63***	−0.43***
Calcite	−0.28***	ns	−0.65***	−0.53***
Dolomite	−0.30***	ns	−0.55***	−0.42***
Total carbonates	−0.31***	ns	−0.66***	−0.53***
Soil loss (−) or gain (+) by				
Tillage erosion (Mg ha⁻¹ yr⁻¹)	0.19**¶	ns	0.56***	0.48***
Water erosion (Mg ha⁻¹ yr⁻¹)	0.12*	ns	0.30***	0.20***
Tillage and water erosion (Mg ha⁻¹ yr⁻¹)	0.19**	ns	0.53***	0.41***

* Correlation is significant at the 0.05 level (two-tailed).

** Correlation is significant at the 0.01 level (two-tailed).

*** Correlation is significant at the 0.001 level (two-tailed).

† Soil organic carbon sorption coefficient.

‡ Soil organic carbon.

§ ns, correlation is not significant at the 0.05 level.

¶ A positive correlation represents an association between soil deposition and sorption coefficients.

The addition of terrain attributes to soil properties strongly improved the prediction of 2,4-D sorption coefficients across the field (Table 5).

The glyphosate K_d was significantly larger in mid- and lower slopes than in upper slopes (Table 2). The glyphosate K_{oc} was significantly larger in mid-slopes than lower and upper slopes. The distribution patterns of glyphosate sorption across the field (Fig. 1H and 1I) were very different from the distribution patterns of the 2,4-D sorption values (Fig. 1A and 1B), soil properties (Fig. 1C, 1D, and 1F), soil loss or gain by tillage and water erosion (Fig. 1E), and CTI (Fig. 1G). Except for some weak associations, there were no significant associations between glyphosate sorption parameters and other variables (Tables 3 and 4). None of the regression models was a strong predictor of glyphosate sorption in soil (Table 5).

Discussion

The strength of 2,4-D sorption was generally low when compared with surface soils in other cultivated prairie landscapes (Farenhorst et al., 2003; Gaultier et al., 2006). This, combined with overall large water erosion rates, leads us to believe that 2,4-D is relatively mobile by runoff and water-eroded soil across this field and could contaminate surrounding waterways if high rainfall occurs soon after 2,4-D application.

The difference in SOCs between upper slopes and lower slopes was on average only 1.5 g kg⁻¹, but the 2,4-D sorption coefficient was on average 1.8 times less in upper slopes than in lower slopes. It is possible that such variations in K_d values are important because by only changing the herbicide sorption coefficient by a factor of two, the predicted amount of herbicides leached in a soil changes by a factor of 10 (Boesten and van der Linden, 1991).

Table 4. Pearson correlation coefficients for determining the association between terrain attributes and other parameters (sorption coefficients, a range of soil properties, or agri-environmental variables).

	Z†	G	A	PROFILE	PLAN	MEAN	SCA	SDA	CTI	SPI
Sorption coefficients										
2,4-D K_d	−0.36***	−0.48***	ns	−0.24***	−0.42***	−0.43***	0.33***	−0.24***	0.59***	0.26
2,4-D K_{oc}	−0.30***	−0.29***	ns	−0.24***	−0.38***	−0.39***	0.30***	−0.20***	0.50***	0.24
Glyphosate K_d	−0.18**	ns	ns	−0.18**	ns	ns	ns	ns	ns	ns
Glyphosate K_{oc}	ns	0.25***	ns	−0.16**	ns	ns	ns	ns	ns	ns
Soil properties										
SOC‡	−0.15**	−0.36***	ns	ns	−0.17**	−0.17**	0.13*	ns	0.26***	ns
Soil pH	0.27***	0.41***	ns	ns	0.15**	0.15**	−0.14*	0.14*	−0.39***	ns
Calcite	0.29***	0.40***	ns	0.25***	0.26***	0.27***	−0.16**	0.19***	−0.43***	ns
Dolomite	0.33***	0.33***	ns	0.28***	0.27***	0.28***	−0.22***	0.12*	−0.44***	−0.17**
Total carbonates	0.33***	0.40***	ns	0.28***	0.29***	0.30***	−0.20***	0.18**	−0.47***	−0.14*
Soil loss (−) or gain (+) by										
Tillage erosion	−0.43***	−0.18**	ns	−0.56***	−0.65***	−0.66***	0.39***	−0.38***	0.60***	0.41
Water erosion	−0.23***	−0.53***	ns	ns	ns	ns	0.25***	ns	0.35***	ns
Tillage + water erosion	−0.40***	−0.51***	0.12*	−0.35***	−0.37***	−0.39***	0.40***	−0.28***	0.59***	0.26

* Correlation is significant at the 0.05 level (two-tailed).

** Correlation is significant at the 0.01 level (two-tailed).

*** Correlation is significant at the 0.001 level (two-tailed). ns, correlation is not significant at the 0.05 level.

† Abbreviations of terrain attributes are explained in Table 1.
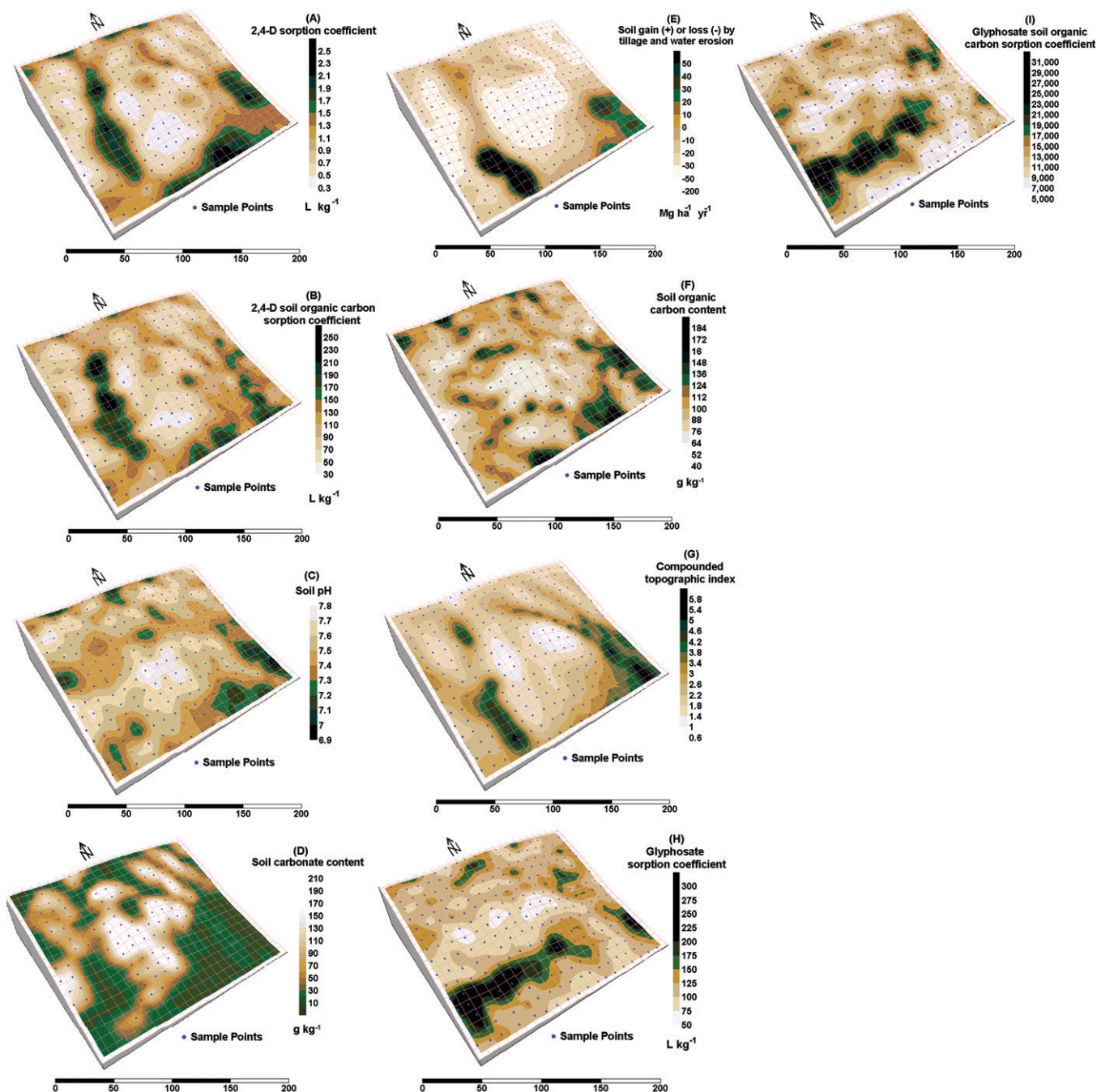
‡ Soil organic carbon.

Fig. 1. The patterns of the distribution of the (A) 2,4-D sorption coefficient (L kg⁻¹), (B) 2,4-D soil organic carbon (SOC) sorption coefficient, (C) soil pH, (D) soil carbonate content (g kg⁻¹), (E) soil loss (−) or gain (+) by tillage + water erosion (Mg ha⁻¹ yr⁻¹), (F) SOC content (g kg⁻¹), (G) compounded topographic index, (H) glyphosate sorption coefficient (L kg⁻¹), and (I) glyphosate SOC sorption coefficient across the study site. The unit of scale bars is meters.

In an undulating to hummocky, calcareous prairie landscape in Manitoba, Canada, the 2,4-D K_d in the Ap-horizon was on average 3 times greater in lower slopes (6.0 L kg⁻¹) than in upper slopes (2.0 L kg⁻¹), whereas the SOC was on average 2.6 times greater in lower slopes (26 g kg⁻¹) than in upper slopes (10 g kg⁻¹) (Gaultier et al., 2006). Landform segments have been incorporated in Canada into the NSDB. Thus, input parameters such as sorption coefficients could be adjusted by using appropriate 2,4-D sorption coefficients for specific classes of landform segments. Based on our

current study and previous results (Gaultier et al., 2006), the value of 2,4-D sorption coefficients should be about a factor of 1.8 to 3 greater in lower slopes than in upper slopes.

Soil carbonate content was more than 5 times greater in upper slopes than in lower slopes. Tillage operations seemed to increase the carbonate content of top soil by redistributing soil from convex to concave areas, thus exposing and incorporating calcareous subsoil materials into the surface layer of upper slopes. As in another calcareous prairie landscape (Gaultier et al., 2006), 2,4-D

Table 5. The most suitable models to predict herbicide sorption coefficients following forward stepwise multiple linear regression and various sets of independent variables. Significant levels are $P < 0.001$ in all cases. The most suitable model (best prediction) was determined to be the model with a relatively large R^2 value and its Cp (Mallows, 1973) closest to the number of variables added, thereby preventing overfitting and colinearity in regression. Variables in the model had to be significant at the 0.05 level.

Variables	Prediction model (coefficient of determination)
2,4-D K_d	
Soil properties	-4.0×10^{-3} total carbonates $- 0.9$ soil pH $+ 4.0 \times 10^{-2}$ SOC $+ 7.7$ ($R^2 = 0.58$)
Terrain attributes	-0.1 G $- 0.1$ PLAN $- 0.1$ MEAN $+ 22.5$ ($R^2 = 0.54$)
Soil + Terrain	2.0×10^{-2} SOC $- 0.7$ Soil pH $- 2.0 \times 10^{-3}$ total carbonates $- 6.9 \times 10^{-2}$ G $- 7.8 \times 10^{-2}$ PLAN $- 5.8 \times 10^{-2}$ MEAN $+ 17.1$ ($R^2 = 0.68$)
2,4-D K_{oc}	
Soil properties	-4.0×10^{-2} total carbonates $- 82.7$ soil pH $- 7.1$ SOC $+ 820.4$ ($R^2 = 0.45$)
Terrain attributes	20.2 CTI $- 6.8$ PLAN $- 2.0 \times 10^{-2}$ SPI $- 4.6$ MEAN ($R^2 = 0.33$)
Soil + Terrain	-0.2 total carbonates $- 8.7$ SOC $- 63.1$ Soil pH $- 8.7$ PLAN $- 7.1$ G $- 6.1$ MEAN $+ 1804.8$ ($R^2 = 0.60$)
Glyphosate K_d	
Soil properties	-0.2 total carbonates $+ 133.6$ ($R^2 = 0.09$)
Terrain attributes	-2.6 Z $+ 1029.7$ ($R^2 = 0.03$)
Soil + Terrain	-0.2 total carbonates $+ 4.6$ G $+ 118.4$ ($R^2 = 0.11$)
Glyphosate K_{oc}	
Soil properties	$-1,156.1$ SOC $- 22.1$ total carbonates $+ 25,682$ ($R^2 = 0.33$)
Terrain attributes	898.1 G $- 8028.2$ PROFILE $+ 9408.4$ ($R^2 = 0.08$)
Soil + Terrain	-1079.4 SOC $- 26.6$ total carbonates $+ 645.8$ G $+ 22,719$ ($R^2 = 0.37$)

sorption had a significant negative association with carbonate content, suggesting that soil calcite and dolomite interfered with the sorption of 2,4-D by soil. Thus, convex terrain forms with increased tillage erosion had lesser 2,4-D sorption by soil than concave terrain forms with lesser tillage erosion or soil deposition. Duchaufour (1976) demonstrated that carbonates in soil could reduce soil organic matter mineralization by forming calcium–organic linkages. In addition, soils saturated with multivalent cations such as Ca^{2+} and Mg^{2+}, the clay–organic complexes tend to be more condensed due to flocculation of clay (Baldock and Nelson, 2000). These two processes could have reduced the sorption capacity of soil organic matter and could explain why the affinity of 2,4-D for soil organic matter decreased with increasing soil pH even though the observed soil pH was well above the 2,4-D dissociation constant (pKa = 2.64) (Ahrens, 1994).

The association between terrain attributes and 2,4-D sorption partition coefficients suggests that topography in these landscapes has an impact on soil properties that affect the extent of 2,4-D sorption by soil. This could include the soil properties that were measured in this study or other soil properties, such as soil organic matter characteristics (Farenhorst, 2006). Similar to in a zero-tilled field (Farenhorst et al., 2003), 2,4-D sorption by soil was much better predicted using terrain and soil properties data than using soil properties data alone. Although the effect of terrain morphology was strong for 2,4-D sorption, the association between terrain attributes and glyphosate sorption was very weak. This is the first report on the spatial variability of glyphosate in a soil landscape, and additional studies in different terrains should confirm whether morphological features indeed have a small impact on explaining the strength of glyphosate by soil. There was also a weak association between measured soil properties and glyphosate sorption. However, there were distinct areas of stronger and weaker glyphosate sorption in the field, possibly as a result of soil properties that were not considered here. This could include differences across the field in soil phos-phate, aluminium oxides, and iron oxides content (De Jonge et al., 2001; Hill, 2001; Gimsing and Borggaard, 2002).

Conclusion

Sorption coefficients are among the most sensitive input parameters in pesticide fate models, and accounting for the variation in sorption coefficients within soil-landscapes could reduce uncertainties in pesticide environmental risk assessments when scaling up from the landscape scale to regional and national scales. Landform segments developed for Canadian prairie landscapes have been incorporated into the NSDB of Canada; therefore, simulations of pesticide fate models could take into account the morphological variations that exist in sorption coefficients at the landscape scale. The results described in this paper suggest that such an approach may be important for some pesticides because 2,4-D sorption coefficients were almost two times greater in lower slopes than upper slopes in this heavily eroded agricultural field. However, in this same terrain, the distribution of glyphosate sorption coefficients across the field was not strongly influenced by terrain attributes or terrain segmentation. Therefore, additional studies are required to compare different terrain forms with a wider range of pesticides to more fully understand the use of digital terrain models in improving estimates of the distribution of sorption coefficients in soil landscapes and how this information will benefit scaling pesticide fate models from the landscape scale to regional scales.

Acknowledgments

and Dr. Ross McQueen, University of Manitoba, for their comments on an earlier draft of this manuscript.

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